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Effect of Adding P and S on the Availability of Mo, P, and S in the Soil with Spinach*

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ABSTRACT

A field experiment in silty loam soil was conducted in the fall of 2022 at the College of Agricultural Engineering Sciences – University of Baghdad in Jadriyah. To investigate the effect of adding Molybdenum, phosphorus, and sulfur on the availability of molybdenum in the soil with spinach. Factorial experiment was conducted according to the arrangement of a split-split plot and the treatments were randomly distributed according to the RCBD. Three levels of molybdenum were 0, 0.5, 1 kg Mo ha^{-1} and its symbols Mo0, Mo_1, and Mo_2. Sulfur levels were 6 and 12 kg S ha^{-1} and its symbols S1 and S_2. Two levels of phosphorus were 18 and 27 kg P ha^{-1} and its symbols P_1 and P_2. The treatments were repeated three times, as well as the comparison treatment without adding any fertilizer so that the number of experimental units became 39 experimental units. The results showed the following. The triple interactions between these nutrients were significant, it gave an increase of 23.3%, 51.1%, 70.1%, 47.4%, 287.3% and 165.8% for available molybdenum, phosphorus, and sulfate in the soil for two cutting, respectively.

Key words: Antagonism، Cutting، Nutrients availability.

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INTRODUCTION

Molybdenum (Mo) is found in soil within primary and secondary minerals and is also adsorbed on the surfaces of iron and aluminum oxides. Additionally, it exists in soil solution and is associated with soil organic matter. Fertile soils are not only capable of supplying nutrients to plants but must also release non-available forms from mineral and organic parts and convert them into available forms to supply plants with the required nutrients over long periods. In contrast, infertile soils require the addition of some nutrients to be able to supply plants with adequate nutrients throughout the growing season. (Mahawash, 2024.). Al-halfi and Al-azzawi, 2022 observed improvements in soil physical properties and increased growth and yield of squash due to the addition of mineral and organic fertilizers. Although molybdenum exists as a negative ion in soil solution, its interactions are similar to those of positive ions. Its mean concentration in the Earth's crust is less than 2 mg kg^{-1} soil, and its concentration in soil ranges between 0.2-5 mg Mo kg^{-1}. Soil minerals controlling molybdate concentration in soil solution include $PbMoO_4$ and $CaMoO_4$.Calcium molybdate predominates in acidic and calcareous soils. Molybdenum interacts with other nutrients; phosphorus enhances molybdenum uptake in plants, through exchange on adsorption surfaces where phosphate replaces molybdate. Conversely, high sulfate ion content in soil solution reduces molybdate uptake in plants. The antagonism between sulfates and molybdates is due to their similar transport mechanisms across cell walls. Sulfur fertilizers in soils with low molybdenum content may exacerbate molybdenum deficiency in plants (Alexandra *et al*, 2011; El-Sayed, *et al*. 2017; Havlin, *et al*., 2017) Plants sensitive to molybdenum deficiency include alfalfa, broccoli, cauliflower, clover, legumes, lettuce, onions

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and spinach, while non-sensitive plants include corn, cotton, carrots, and barley (Havlin, *et al*., 2017). Spinach (*Spinacia oleracea*) belongs to the Amaranthaceae family. It is an annual leafy vegetable (Al-Hilu, 1999). Native to central and western Asia (Barzegar *et al*., 2007.). Growing up to 30 cm tall and consumed raw or cooked. It contains vitamins A, B, C, K, folic acid, magnesium, iron, and calcium. Spinach grows at temperatures between 10-21°C and can be harvested 45-90 days after planting, depending on the variety. It is grown in both spring and fall seasons. Fresh spinach contains 91 g water, 3.6 g carbohydrates, 0.4 g sugar, 2.2 g fiber and 2.9 g protein per 100 g (Elvira *et al*., 2019). The study aims to investigate the effect of adding Molybdenum, phosphorus and sulfates on molybdenum availability in soil and with spinach plants.

MATERIALS AND METHODS

A field experiment was conducted in the fall season of 2022 at the Agricultural Research Station of the College of Agricultural Engineering Sciences, University of Baghdad, in the Jadriya, in silty loam soil. Soil samples were taken from the field at a depth of 0-30 cm from various locations. Table (1) shows some physical and chemical properties of the field soil before planting. Soil properties were estimated according to (Black, 1965a; Page *et al* 1982; Pratt, 1965; Wodaje and Abebaw, 2017) The factorial experiment was conducted according to the split-split plot arrangement, and treatments were randomly distributed according to the randomized complete block design (RCBD). Molybdenum levels were placed in the sub-sub plots at three levels: 0, 0.5, and 1kg Mo ha^{-1} in the form of ammonium molybdate denoted as Mo_0, Mo_1, and Mo_2. Sulfur levels were placed in the sub plots at two levels: 6 and 12 kg S ha^{-1} in the form of potassium sulfate, denoted as S_1 and S_2. Phosphorus levels were placed in the main plots at two levels: 18 and 27 kg P ha^{-1} in the form of di ammonium phosphate, denoted as P_1 and P_2. The treatments were replicated three times, in addition to a control treatment without any fertilizer, making the total number of experimental units 39. The study parameters included estimating the available molybdenum, phosphorus and sulphate in the soil immediately after the first and second harvests.

Table 1. Some chemical, physical, and fertility properties of the field soil before planting

Property	Value	Unit of Measurement
$EC_{1:1}$	2.32	dS m^{-1}
$pH_{1:1}$	7.52	-
Cation Exchange Capacity	17.3	$Cmol_+$ kg^{-1} soil
Organic Matter	9.8	g kg^{-1}
Carbonate Minerals	260.1	
Soluble Calcium	5.24	
Soluble Magnesium	3.725	
Soluble Sodium	1.465	
Soluble Potassium	0.51	m mol L^{-1}
Soluble Chloride	7.13	
Soluble Sulfates	2.45	
Soluble Bicarbonates	1.625	
Soluble Carbonates	Nil	
Available Nitrogen	20.12	
Available Phosphorus	8.19	mg kg^{-1}
Available Potassium	176.0	
Available Sulfates	180.8	
Available Molybdenum	2.55	
Sand	354.0	
Silt	522.0	g kg^{-1}
Clay	124.0	
Texture	Silty Loam	

RESULTS AND DISCUSSION

The statistical analysis of the results in Table (2) shows a significant effect of the added molybdenum levels on its availability. The highest concentration was for the Mo_2 treatment, with a mean of 2.95 mg kg^{-1} soil,

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and the lowest mean was 2.23 mg kg^{-1} soil in the Mo_0 treatment, an increase of 32.3%. Phosphorus and sulfur levels did not have a significant effect on the available molybdenum. However, the interaction between phosphorus and sulfur had a significant effect on the available molybdenum, especially the interaction between P_1S_2, which gave the highest mean of 2.6 mg kg^{-1} soil. The interaction between molybdenum and phosphorus was significant, with the P_2Mo_2 treatment giving the highest mean 2.98 mg kg^{-1} soil compared to the lowest mean in the P_2Mo_0 treatment, which gave 2.18 mg kg^{-1} soil an increase 36.7%. The interaction between molybdenum and sulfur was significant, with the S_2Mo_2 treatment giving the highest mean 2.99 mg kg^{-1} soil compared to the lowest mean 2.16 mg kg^{-1} soil in the S_2Mo_0 treatment. The triple interaction was significant, giving the highest mean 3.02 mg kg^{-1} soil in the $P_1S_2Mo_2$ treatment compared to the control treatment $P_0S_0Mo_0$, which gave a mean 2.45 mg kg^{-1} soil, an increase 23.3%. It also outperformed the interactions of phosphorus with sulfur in the absence of molybdenum and the presence of its first level.

Table 2. Effect of adding Mo, P and S on available Molybdenum in first harvest (mg kg^{-1} soil)

P	**S**	**Mo**			**P *S**
		Mo0	**Mo1**	**Mo2**	
P1	S1	2.37	2.41	2.82	2.53
	S2	2.20	2.57	3.02	2.60
P2	S1	2.23	2.48	3.01	2.58
	S2	2.12	2.33	2.95	2.47
Control			2.450		
LSD P*S*Mo			0.106		LSD P*S 0.093
			P * Mo		
P		Mo0	Mo1	Mo2	P mean
P1		2.28	2.49	2.92	2.56
P2		2.18	2.41	2.98	2.52
LSD P*Mo			0.089		LSD P N.S
			S*Mo		
S		Mo0	Mo1	Mo2	S mean
S1		2.3	2.44	2.92	2.55
S2		2.16	2.45	2.99	2.53
LSD S*Mo			0.075		LSD S N.S
			Mo		
Mo levels		Mo0	Mo1	Mo2	
Mo mean		2.23	2.45	2.95	
LSD 0.05 Mo			0.063		

The statistical analysis of the results in Table (3) show a significant effect of the added molybdenum levels on its availability. The highest value was for the Mo_2 treatment, with a mean 3.22 mg kg^{-1} soil and the lowest mean was 2.24 mg kg^{-1} soil in the Mo_0 treatment, an increase 43.8%. Phosphorus and sulfur levels did not have a significant effect on the available molybdenum in the soil. Additionally, the interaction between phosphorus and sulfur did not have a significant effect on the available molybdenum.

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Table 3. Concentration of available Molybdenum in the soil in the second harvest (mg kg^{-1})

P	S	Mo			P *S	
		Mo0	Mo1	Mo2		
P1	S1	2.29	2.57	3.44	2.77	
	S2	2.17	2.86	2.96	2.66	
P2	S1	2.34	2.50	2.98	2.60	
	S2	2.14	2.89	3.52	2.85	
Control			2.330			
LSD P*S*Mo			0.309		LSD P*S	N.S
			P * Mo			
P		Mo0	Mo1	Mo2	P mean	
P1		2.23	2.72	3.2	2.72	
P2		2.24	2.69	3.25	2.73	
LSD P*Mo			N.S		LSD P	N.S
			S*Mo			
S		Mo0	Mo1	Mo2	S mean	
S1		2.32	2.54	3.21	2.69	
S2		2.16	2.87	3.24	2.75	
LSD S*Mo			0.219		LSD S	N.S
			Mo			
Mo levels		Mo0	Mo1	Mo2		
Mo mean		2.24	2.71	3.22		
LSD Mo			0.151			

The interaction between molybdenum and phosphorus was not significant. However, the interaction between molybdenum and sulfur was significant, with the S_2Mo_2 treatment giving the highest mean 3.24 mg kg^{-1} soil compared to the lowest mean 2.16 mg kg^{-1} soil in the S_2Mo_0 treatment. The triple interaction was significant, giving the highest mean of 3.52 mg kg^{-1} soil in the $P_2S_2Mo_2$ treatment compared to the control treatment $P_0S_0Mo_0$, which gave a mean 2.33 mg kg^{-1} soil an increase 51.1%. It also outperformed the interactions of phosphorus with sulfur in the absence of molybdenum and the presence of its first level.

Table 4. Concentration of available Phosphorus in the soil in the first harvest (mg kg^{-1})

P	S	Mo			P *S	
		Mo0	Mo1	Mo2		
P1	S1	10.70	10.30	11.30	10.80	
	S2	10.50	11.10	10.40	10.60	
P2	S1	12.30	10.80	11.70	11.60	
	S2	10.50	11.10	13.10	11.60	
Control			7.70			
LSD P*S*Mo			1.41		LSD P*S	N.S
			P * Mo			
P		Mo0	Mo1	Mo2	P mean	
P1		10.60	10.70	10.80	10.70	
P2		11.40	10.90	12.40	11.60	
LSD P*Mo			N.S		LSD P	0.55
			S*Mo			
S		Mo0	Mo1	Mo2	S mean	
S1		11.50	10.60	11.50	11.20	
S2		10.50	11.10	11.70	11.10	
LSD S*Mo			N.S		LSD S	N.S
			Mo			
Mo levels		Mo0	Mo1	Mo2		
Mo mean		11.00	10.80	11.60		
LSD Mo			0.52			

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The statistical analysis of the results in Table (4) shows a significant effect of the added molybdenum levels on the availability of phosphorus. The highest concentration was for the Mo_2 treatment, with a mean 11.6 mg kg^{-1} soil an increase 8.4% compared to the P_1 level. Sulfur levels did not have a significant effect on the available phosphorus and the interaction between phosphorus and sulfur did not have a significant effect on the availability of phosphorus. The interaction between molybdenum and phosphorus, molybdenum and sulfur was not significant. The triple interaction was significant, giving the highest mean 13.10 mg kg^{-1} soil in the $P_2S_2Mo_2$ treatment compared to the control treatment $P_0S_0Mo_0$, which gave a mean of 7.70 mg kg^{-1} soil an increase of 70.1%. It also outperformed most interactions of phosphorus with sulfur in the absence of molybdenum, except for the $P_2S_1Mo_0$ treatment and the first level of molybdenum in its entirety, and the second level of molybdenum except for the $P_2S_1Mo_2$ treatment. The statistical analysis of the results in Table (5) shows no significant effect of the added Mo, P, and S on the availability of phosphorus. Phosphorus levels had a significant effect on the available phosphorus in the soil, with the P_2 treatment giving the highest mean 10.8 mg kg^{-1} soil an increase 6.9% compared to the P_1 level. The triple interaction was significant, giving the highest mean of 11.2 mg kg^{-1} soil in the $P_2S_1Mo_1$ treatment compared to the control treatment $P_0S_0Mo_0$, which gave a mean of 7.6 mg kg^{-1} soil an increase 47.4%. The differences were not significant between this treatment and the rest of the triple interaction treatments, except for the $P_1S_1Mo_0$ and $P_1S_1Mo_2$ treatments

Table 5. Concentration of available Phosphorus in the Soil in the second harvest (mg kg^{-1})

P	S	Mo			P *S	
		Mo0	Mo1	Mo2		
P1	S1	9.50	10.40	9.50	9.80	
	S2	10.90	10.40	9.90	10.40	
P2	S1	10.40	10.60	10.90	10.70	
	S2	10.70	11.20	10.90	11.00	
Control			7.60			
LSD P*S*Mo			1.33		LSD P*S	N.S
			P * Mo			
P		Mo0	Mo1	Mo2	P mean	
P1		10.20	10.40	9.70	10.10	
P2		10.60	10.90	10.90	10.80	
LSD P*Mo			N.S		LSD P	0.41
			S*Mo			
S		Mo0	Mo1	Mo2	S mean	
S1		10.00	10.50	10.20	10.20	
S2		10.80	10.80	10.40	10.70	
LSD S*Mo			N.S		LSD S	N.S
			Mo			
Mo levels		Mo0	Mo1	Mo2		
Mo mean		10.40	10.70	10.30		
LSD Mo			N.S			

The statistical analysis of the results in Table (6) shows no significant effect of the added Mo, P, and S on the availability of sulfates. Triple interaction was significant, with the $P_2S_2Mo_1$ treatment giving the highest mean 635.2 mg kg^{-1} soil compared to the control treatment $P_0S_0Mo_0$, which gave a mean 164.0 mg kg^{-1} soil an increase 287.3%. The differences were significant between this treatment and the rest of the triple interaction treatments, except for the $P_1S_2Mo_0$, $P_2S_2Mo_0$, $P_1S_2Mo_2$, and $P_2S_1Mo_2$ treatments.

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Table 6. Concentration of available Sulfates in the Soil in the first harvest (mg kg^{-1})

P	S	Mo			P *S	
		Mo0	Mo1	Mo2		
P1	S1	561.6	522.1	521.6	535.1	
	S2	579.2	534.9	597.9	570.7	
P2	S1	559.5	523.7	588.3	557.2	
	S2	566.4	635.2	551.5	584.4	
Control			164.0			
LSD P*S*Mo			73.2		LSD P*S	N.S
			P * Mo			
P		Mo0	Mo1	Mo2	P mean	
P1		570.4	528.5	559.7	552.9	
P2		562.9	579.5	569.9	570.8	
LSD P*Mo			N.S		LSD P	N.S
			S*Mo			
S		Mo0	Mo1	Mo2	S mean	
S1		560.5	522.9	554.9	546.1	
S2		572.8	585.1	574.7	577.5	
LSD S*Mo			N.S		LSD S	N.S
			Mo			
Mo levels		Mo0	Mo1	Mo2		
Mo mean		566.7	554.0	564.8		
LSD Mo			N.S			

The statistical analysis of the results in Table (7) shows no significant effect of the added Mo, P, and S levels on the availability of sulfates. Sulfur levels had a significant effect on the available sulfates, with the S_2 treatment recording the highest mean 364.1 mg kg^{-1} soil an increase 10.2% compared to the S_1 treatment. The interaction between phosphorus and sulfur, phosphorus and molybdenum did not have a significant effect on the available sulfates. The S_2Mo_0 treatment recorded the highest value 404.1 mg kg^{-1} soil while the S_1Mo_1 treatment recorded the lowest value 318.7 mg kg^{-1} soil an increase 26.8%. The triple interaction was significant, with the $P_1S_2Mo_0$ treatment giving the highest mean 404.8 mg kg^{-1} soil compared to the control treatment $P_0S_0Mo_0$, which gave a mean 152.3 mg kg^{-1} soil an increase 165.8%. The differences were significant between this treatment and some of the other triple Interaction treatments.

Table 7. Concentration of available Sulfates in the Soil in the second harvest (mg kg^{-1})

P	S	Mo			P *S	
		Mo0	Mo1	Mo2		
P1	S1	361.6	285.9	326.4	**324.6**	
	S2	404.8	363.7	307.7	**358.8**	
P2	S1	302.4	351.5	355.2	**336.4**	
	S2	403.5	372.3	332.8	**369.5**	
Control			152.3			
LSD P*S*Mo			59.1		**LSD P*S**	**N.S**
			P * Mo			
P		Mo0	Mo1	Mo2	**P mean**	
P1		383.2	324.8	317.1	**341.7**	
P2		352.9	361.9	344.0	**352.9**	
LSD P*Mo			N.S		**LSD P**	**N.S**
			S*Mo			
S		Mo0	Mo1	Mo2	**S mean**	
S1		332.0	318.7	340.8	**330.5**	
S2		404.1	368.0	320.3	**364.1**	
LSD S*Mo			41.8		**LSD S**	**17.9**
			Mo			
Mo levels		Mo0	Mo1	Mo2		
Mo mean		368.1	343.3	330.5		
LSD Mo			N.S			

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From the data in tables 2, 3, 4, 5, 6, and 7, it is observed that the available molybdenum in the soil increased with higher levels of added molybdenum, which is expected. Additionally, the concentration in the second harvest was higher than in the first, confirming increased availability in alkaline pH (Havlin e*t al*.,2017). The triple interaction also led to increased available molybdenum, due to the replacement of adsorbed molybdate by orthophosphate and sulfate, thus releasing it into the soil solution (Havlin e*t al*.,2017). Phosphorus levels increased the available phosphorus in the soil in both harvests, which is natural. (Khudhair and Abdulrasool, 2023) reported an increase in eggplant yield and phosphorus concentration in fruits and vegetative parts with phosphorus fertilization, along with N and K levels. Increased nutrient availability in the soil and potato growth and yield with the addition of mineral fertilizers and vermicompost. Observed increased growth and yield of cauliflower with the addition of phosphate and bio-fertilizers along with vermicompost. Sulfur levels alone or in combination with phosphorus did not increase available phosphorus, Due to the weak ability of sulfates to replace orthophosphate on adsorption surfaces and thus release it into the soil solution. The interaction between molybdenum and phosphorus or molybdenum and sulfates did not increase available phosphorus, likely because the added molybdenum amount was too small compared to the added or existing phosphorus and sulfur in the soil, preventing it from competing on adsorption surfaces. However, the triple interaction had a positive effect on this trait. The same trend was observed for available sulfates in the soil in the first harvest, except for the triple interaction, where sulfur levels had a positive effect. Sulfur is important for plant growth as it plays a vital and high role in plant nutrition and improves soil fertility along with other nutrients like nitrogen, potassium, and phosphorus . Reported increased availability of N, P and K in the soil and their concentrations in potato tubers with different levels of agricultural sulfur, along with organic and mineral fertilizers. The positive effect of the triple interaction on increasing available phosphorus and sulfates may be due to the synergistic action of these negative anions on adsorption surfaces

CONCLUSION

The results of this study demonstrated that the combined application of molybdenum, phosphorus, and sulfur significantly affected the availability of these nutrients in silty loam soil cultivated with spinach. The triple interaction among these nutrients played an important role in increasing the availability of molybdenum, phosphorus, and sulfate in the soil during both cuttings. These findings highlight the importance of balanced nutrient management in improving soil nutrient availability and enhancing fertilizer efficiency. Therefore, the appropriate combination of molybdenum, phosphorus, and sulfur can contribute to better soil fertility management and provide favorable nutritional conditions for spinach growth.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR/S DECLARATION The authors declare that the work is original and has not been published elsewhere.

AUTHOR'S CONTRIBUTION STATEMENT

The author contributed to the design, implementation, data analysis, and writing of the research.

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تأثير إضافة الفوسفور والكبريت على جاهزية الموليبدنم والفوسفور والكبريت في التربة المزروعة بالسبانخ

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المستخلص

نفذت تجربة حقلية في الموسم الخريفي 2022 في أحد حقول كلية علوم الهندسة الزراعية - جامعة بغداد في مجمع الجادرية في تربة مزيجة غرينية ، لمعرفة تأثير إضافة الموليبدنم والفسفور والكبريت في جاهزية الموليبدنم والفسفور والكبريتات في التربة بوجود السبانخ . نُفذت تجربة عاملية حسب ترتيب الالواح المنشقة – المنشقة ووزعت المعاملات عشوائياً حسب تصميم القطاعات الكاملة المعشاة RCBD . اضيف الموليبدنم بثلاثة مستويات هي 0 و 0.5 و 1 كغم Mo هـ$^{-1}$ ورمز لها Mo_0 و Mo_1 و Mo_2 والكبريت بمستويين هما 6 و12 كغم S هـ$^{-1}$ ورمز لهما S_1 و S_2 والفسفور بمستويين هما 18و27 كغم P هـ$^{-1}$ ورمز لهما P_1 و P_2 . كررت المعاملات ثلاث مرات، فضلا عن معاملة المقارنة من دون إضافة أي سماد، إذ أصبح عدد الوحدات التجريبية 39 وحدة تجريبية . أظهرت النتائج أن التداخل الثلاثي لعوامل الدراسة كان معنوياً في جاهزية المغذيات الثلاثة في التربة، إذ حققت زيادة مقدارها 23.3% و51.1% و70.1% و47.4% و287.3% و165.8 % للموليبدنم والفسفور والكبريتات الجاهزة في التربة للحشتين على التعاقب .

الكلمات المفتاحية: التضاد، الحشات، جاهزية المغذيات.